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Cite as: AIP Conference Proceedings **2126**, 080004 (2019); <https://doi.org/10.1063/1.5117599>  
Published Online: 26 July 2019

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# Hydrogen Monitoring in the Heat Transfer Fluid of Parabolic Trough Plants

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**Abstract.** The hydrogen formation of diphenyl oxide (DPO) / biphenyl (BP) based heat transfer fluids (HTFs) can cause undesirably high concentrations of the gas in the HTF system of solar thermal parabolic trough plants. Hydrogen permeates from the HTF into the vacuum insulation of the heat collecting elements (HCEs). Excessive hydrogen concentrations in the HTF cause early saturation of the getter materials in the HCEs and consequently to high thermal losses when the heat insulation effect of the vacuum gets lost. In order to avoid a “hydrogen problem” the concentration of the gas has to be monitored and controlled in the HTF. In this study hydrogen analysis has been performed with HTF samples that were collected including all dissolved gases using special steel cylinders that were directly connected to the HTF system. The samples were analysed off-line at ambient conditions in a lab applying a combination of pressure measurement and compositional analysis with gas chromatography. The results indicate that under regular operating conditions hydrogen can exceed the specified limit more than hundredfold. Decompression tests in a CSP plant also indicate that hydrogen concentrations can be lowered using ready available components of a parabolic trough plant. Hence, extremely high hydrogen levels can be avoided by sufficient nitrogen exchange.

## INTRODUCTION

The eutectic mixture of diphenyl oxide (DPO) and biphenyl (BP) is the most commonly applied heat transfer fluid (HTF) in parabolic trough power plants [1]. The fluid’s maximum operating temperature is 400°C but slow degradation already occurs within the typical operating range of 293 – 393°C.

Hydrogen is a particularly important degradation product as it permeates into the vacuum insulation of the heat collecting elements (HCEs). The HCEs are equipped with getter materials that reversibly bind hydrogen to avoid the formation of a heat conducting atmosphere inside the HCEs. This insulation lasts as long as the getter capacity is not exceeded. New Schott PTR<sup>®</sup>70 receivers are specified with a residual pressure in the annulus of less than 0.001mbar [2]. The maximum allowable effective hydrogen pressure in the HTF is specified with 30Pa. Burkholder et al. estimated the heat losses of a receiver with 1 Torr (133Pa) of hydrogen inside the annulus would have a heat loss of 3350W at only 350°C compared to only 850W when the vacuum is maintained [3]. These authors also simulated the consequences of an HCE heat loss by a factor of 3 on a parabolic trough plant and concluded that this would cause 20% decrease in annual revenue [3].

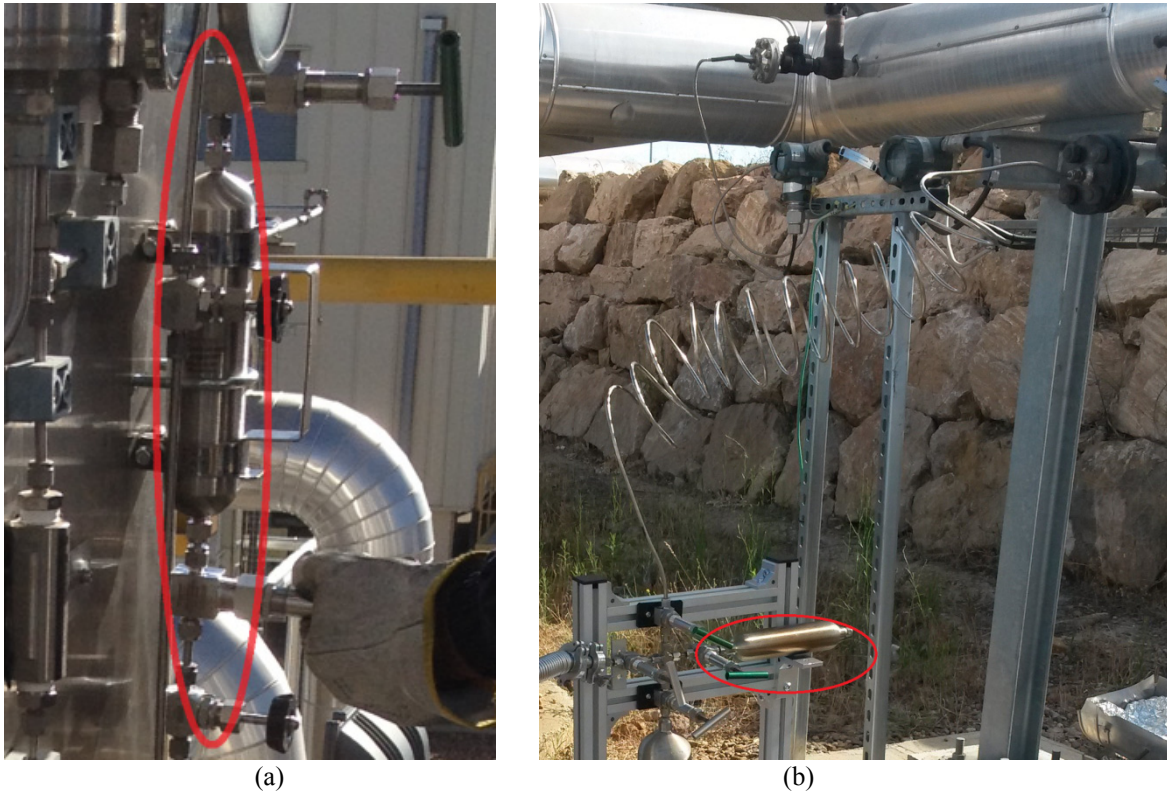
In order to maintain the performance of the HCEs for sufficiently long lifetimes, the hydrogen permeation has to be kept within tolerable limits by controlling the hydrogen concentration in the HTF [4,5]. In contrast to the obvious need for hydrogen monitoring and control, up to now there is neither a standard for off-line hydrogen analysis nor a fully validated hydrogen-sensor based method available.

In this study, the hydrogen concentrations in thirteen solar thermal trough plants have been examined using hot and pressurized HTF samples that were extracted from the systems during operation. The samples have been analysed off-line using a combination of pressure measurement and gas chromatography.

## METHODOLOGY

### Extraction of Representative HTF Samplings from CSP Systems

The analytical procedure used in this study includes the extraction of HTF samples without any changes of fluid and gas composition as a first step. For this purpose, hydrogen-tight steel cylinders equipped with high temperature valves are directly connected to the HTF system. The filling of the samples with HTF is performed via pressurized flushing of HTF in flow-through mode using cylinders with two valves (Fig. 1a), or by filling the pressurized HTF into evacuated cylinders equipped with only one valve (Fig. 1b).



**FIGURE 1.** Filling of hot and pressurized HTF samples into steel cylinders (highlighted with red circles) in flow through mode using nitrogen-filled cylinders with two valves (a) or using evacuated cylinders with only one valve (b).

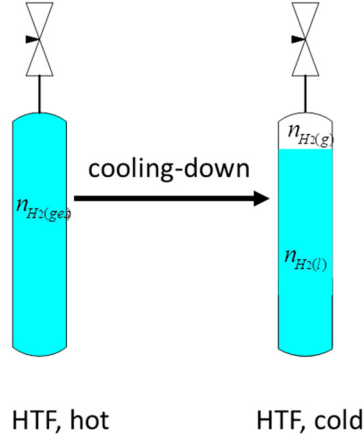
Sampling with the evacuated cylinders requires only one valve per cylinder (Fig. 1b) which saves some material costs. This sampling concept is also flexible as it can be applied at different sites within a CSP plant or even at different CSP plants. Nevertheless, a vacuum rack is required that allows the evacuation of all connection tubing and the extraction of a forerun into a separate cylinder before HTF is filled into the sample cylinder.

Extracting the sampling with the flow-through cylinders requires no vacuum rack (Fig. 1a). As a safety precaution the cylinders are flushed with nitrogen before they are filled with hot HTF. The outflow of the cylinder can be discharged into a waste container after sufficient cooling. This set-up can basically be installed at any point of the HTF system where the supply with cooling fluid and nitrogen can be provided. Alternatively, these cylinders can be filled using a bypass between the cold inlet and the hot outlet of a loop according to the pressure gradient. The latter setup has been established so far in research or demonstration facilities while the other sampling methods have been applied in fourteen commercial scale parabolic trough facilities up to now.

After cooling to ambient conditions, the cylinders are disconnected from the system and shipped to DLR's lab for analytical evaluation.

## Determination of Dissolved Gases

The HTF analysis can be focused on dissolved gases or on any other of the fluid's evaporable ingredients using gas chromatographic techniques adapted to the required analytical parameter. When cooling down, the HTF inside the steel cylinder shrinks due to the increasing density of the fluid (Fig 2).



**FIGURE 2.** Schematic of steel cylinder filling; fully filled in the hot state (left) and partially filled after cooling down (right)

Hence, at ambient conditions the cylinders contain a gaseous and a liquid phase. The gas contents of both phases are considered. The gaseous phase is quantified by determining the pressure above the liquid ( $p_{tot}$ ) via expansion into a calibrated volume that is equipped with temperature and pressure gauges. For calculating the amount of a specific gas like hydrogen in the gaseous phase ( $n_{gas(g)}$ ) according to equation 1 the gas composition ( $x_{gas}$ ) is determined with micro gas chromatography. Furthermore, the volume of the cylinder ( $V_{cyl}$ ) and the mass of HTF ( $m_{HTF}$ ) are measured. The density of the HTF ( $\rho_{HTF}$ ) is to be taken into account as well as the general gas constant ( $R$ ) and the absolute sample temperature ( $T$ ). As so far no evidence has been reported on that the density is subject to changes due to aging effects the data of new *Dowtherm™ A* is used [4,6].

$$n_{H_2(g)} = \frac{p_{tot} x_{H_2} \left( V_{cyl} - \frac{m_{HTF}}{\rho_{HTF}} \right)}{R \cdot T} \quad (1)$$

The gases dissolved inside the liquid phase of a sample are calculated according to equation 2 taking Henry coefficients ( $H_{H_2}$ ) provided by DLR [4] and the average molar mass of the new HTF ( $M_{HTF}$ ) into account. It is assumed that the Henry coefficient does not depend considerably on the aging condition of the fluid. Typically, more than 90% of the hydrogen is found in the gas phase above the liquid sample.

$$n_{H_2(l)} = \frac{p_{H_2} m_{HTF}}{H_{H_2} M_{HTF}} \quad (2)$$

The total amount of hydrogen in the sample is referred to the mass of HTF (molal concentration or molality,  $b_{gas}$ ) according to equation 3 ( $n_{H_2(l)}$  and  $n_{H_2(g)}$  representing the amount in hydrogen in the liquid and in the gas phase of the sample).

$$b_{H_2} = \frac{n_{H_2(l)} + n_{H_2(g)}}{m_{HTF}} \quad (3)$$

Most of the dissolved gas is nitrogen as this is used as protective gas in the HTF system. Hydrogen is the prevailing gaseous trace component. Typically, only very low amounts of other gases like carbon monoxide and methane are found. The concentration levels of oxygen have not been finally clarified so far as particular caution is required during sampling and analysis in order to exclude any contamination of the samples with air.

## Conversion of Hydrogen Concentration into Pressure

The outcome of the gas analysis is the total amount of each gas per mass of HTF sample (typically in  $\mu\text{mol}$  gas per kg HTF). For comparison with the hydrogen concentration limit given by receiver manufacturers in terms of pressure [2], the conversion according to Henry's law as well as the comparison with a hydrogen atmosphere with identical volumetric hydrogen density like in the liquid HTF are considered. The pressure according to Henry's law (4) will doubtlessly be present in a gas phase that is in equilibrium with the HTF.

$$p_{H_2} = H_{H_2} \frac{n_{H_2(l)}}{n_{HTF} + n_{H_2(l)}} \approx H_{H_2} b_{H_2} M_{HTF} \quad (4)$$

During regular plant operation only a negligible amount of gas bubbles is to be expected in the HTF within the solar field. Nevertheless, if equilibrium between the gas phase in the HCEs and the HTF would be reached, the Henry pressure would be reached in the HCEs as well. This is, as the steel tube of the HCE would not directly affect the equilibrium condition.

It is not to be expected that the permeation rate is predominantly driven by the hydrogen pressure in the gas bubbles in the HTF. Most of the permeation should be related to the overall hydrogen density in the HTF as the HCEs are mostly in contact with the liquid HTF. The pressure of an ideal gas with identical volumetric hydrogen density like in the HTF can be calculated according to (5).

$$p_{H_2} = R T b_{H_2} \rho_{HTF} \quad (5)$$

It turns out that the 0.3mbar limit given for the Schott PTR<sup>®</sup>70 receiver corresponds to  $0.8\mu\text{mol/kg}$  according to Henry's law, while a volumetric hydrogen density in the HTF that equals gaseous hydrogen of 0.3mbar is achieved within the liquid HTF at about  $8\mu\text{mol/kg}$ . Hence, the ideal gas criterion would result in an about 10 times less strict maximum allowable hydrogen limit compared to the Henry criterion. Studies on the permeation of hydrogen from the HTF through receiver tubes have to be performed to decide which conversion matches the permeation rate according to the effective pressure indicated by *Schott*.

## RESULTS AND DISCUSSION

### Hydrogen Concentration Changes within the HTF system

#### *Changes within a Day*

The variation of hydrogen within individual operation days was analysed by extracting a set of samples during the day. The sampling frequency can be as high as six cylinders per hour. In many cases five cylinders had been filled within a day and had been evaluated subsequently in terms of hydrogen within less than two weeks' time after the samples were collected.

According to Fig. 3 each CSP plant studied exceeds the hydrogen limit for PTR 70 receivers considerably irrespective of the question how the conversion from concentration into pressure units should be done. Up to  $114\mu\text{mol/kg}$  were detected which is more than 140 times the limit of  $0.8\mu\text{mol/h}$ .

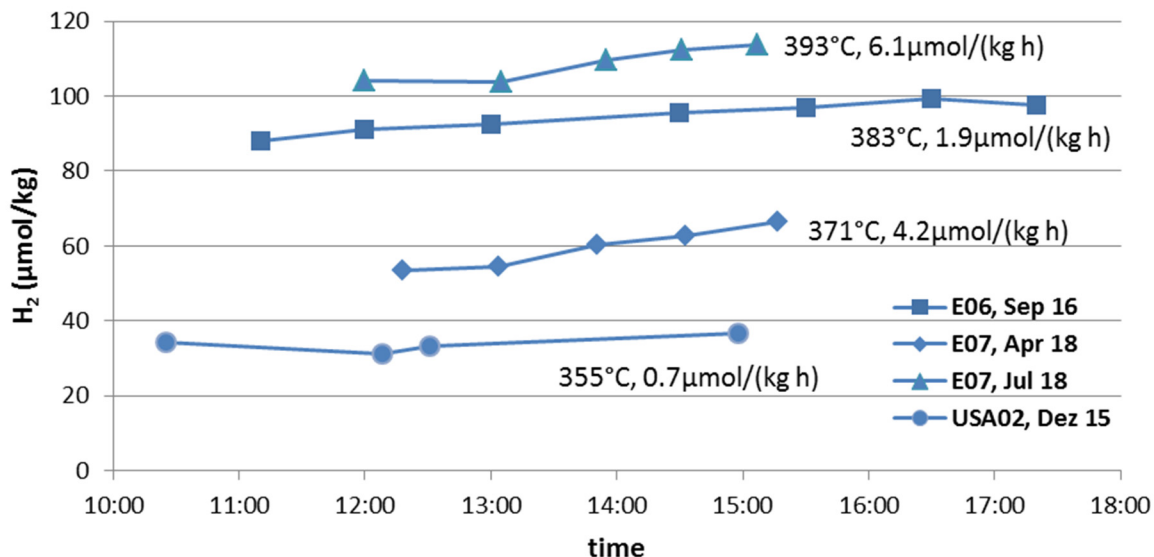
In general, higher concentrations are found at higher operation temperatures. A slight, but steady rise of concentration can be observed during the day in particular at higher operation temperatures and when cloudless conditions prevail.

The rise basically correlates with the field outlet temperature. Nevertheless, the correlation holds not strictly when different plants are compared (Fig. 4). This is as the hydrogen concentration depends not alone on the hydrogen formation but also on the distribution in the system and on loss mechanisms. In addition, the hydrogen formation rate depends also on the condition of the HTF. The rate increases steadily with progressing operation time. This feature is in contrast to silicone fluids which reveal much slower and constant hydrogen formation rates considering the long-term behavior [7].

The formation of hydrogen will mostly take place in the hot header and the tubing before the heat exchanger as the decomposition depends exponentially on the temperature. Hence, the specific header volume of a CSP plant in

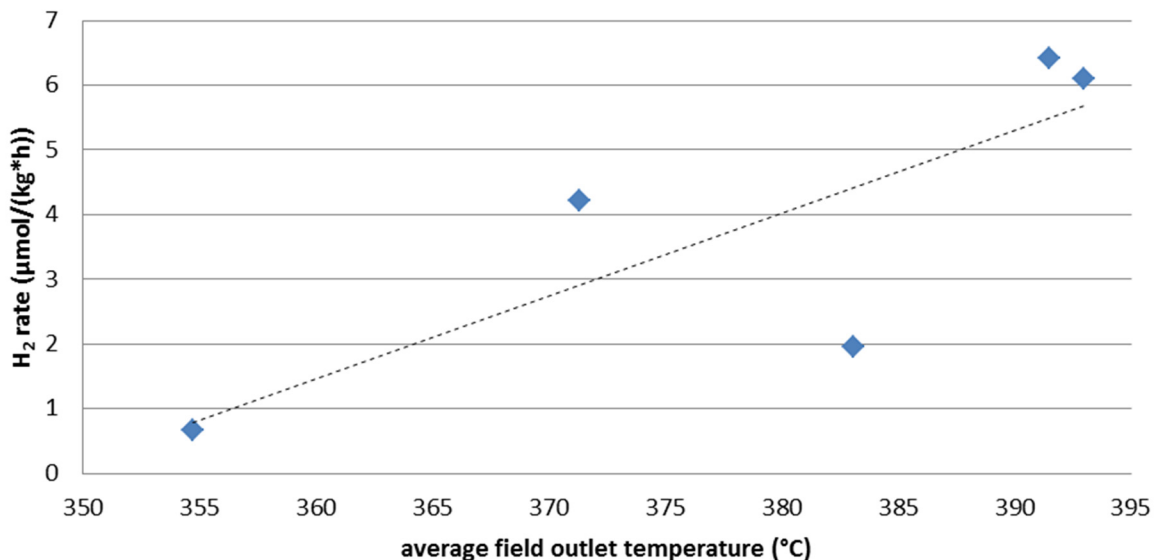


relation to the overall HTF volume will have a major impact on the concentration change. In addition, the hydrogen formation rate depends on the condition of the HTF as the formation increases in used HTF qualities.



**FIGURE 3.** Measured hydrogen concentrations at three different CSP plants within a day (with indication of the average field outlet temperatures and the average increases of hydrogen).

Besides the differences in terms of hydrogen distribution within the total HTF volume there can be also differences in terms of hydrogen distribution between the fluid and the gas phase. The latter will be available in the expansion and overflow vessels. Another difference arises from hydrogen losses. Possible hydrogen losses are leakages in seals like ball-joint connections in the solar field. Although the permeation into the HCEs is a threat to these components it is so slow that it won't affect the hydrogen concentration in the HTF in a measurable manner.



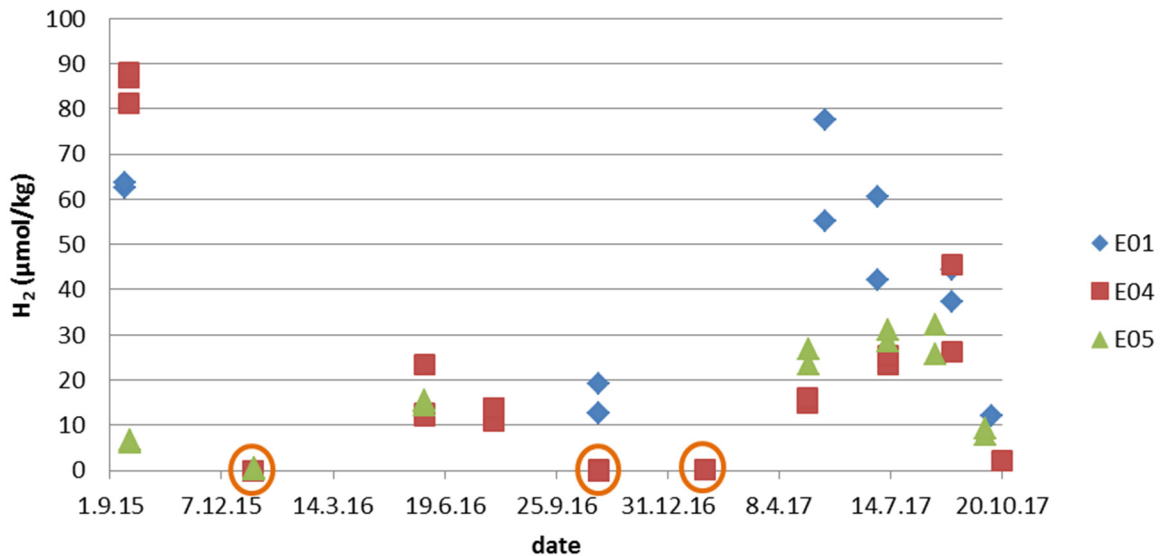
**FIGURE 4.** Correlation of the daily hydrogen increase rates with the average field outlet temperature (data taken from five days at four different plants).

### Seasonal Variations

Most measurements have been performed in Spain so far. Usually, two or three samples were analysed that had been extracted typically around noon time.

In the case of Spain the daily operation hours and the maximum operation temperatures decrease considerably in the winter months. In summer, long periods with temperatures close to the stability limit of DPO/BP can be achieved. This is reflected by the hydrogen concentrations that generally decrease in winter and then rise again in summer (Fig. 5).

Out of the 160 samples that have been analysed so far only the ones collected at four dates in winter revealed less hydrogen as required to comply with the limit for the Schott PTR<sup>®</sup>70 receiver (marked with orange circles in figure 5). In these cases, the hydrogen formation was very low due to low HTF temperatures and short operation intervals. Obviously, the venting losses exceeded the formation of hydrogen in these specific situations.



**FIGURE 5.** Hydrogen concentration at three different CSP plants in Spain within a period of about two years (orange circles mark data below the hydrogen limit for the Schott PTR 70 receiver).

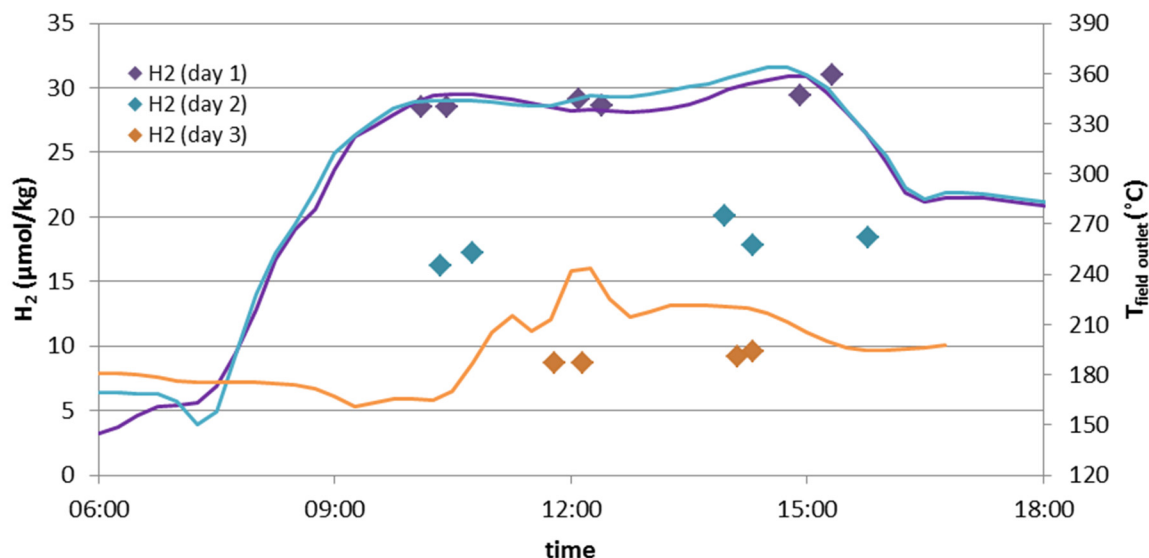
### Analysis of Active Elimination of Hydrogen from the HTF System

As long as hydrogen is not removed from the HTF system it will accumulate and build up the critical concentrations that have been observed in more than 90% of all samples which have been analysed so far at DLR. This is as the only loss mechanisms are permeation through hot steel piping or through sealed connections like ball-joints as long as the system is operated without deliberate gas exchange.

Several authors like *Kuckelkorn et al.*, *Lang et al.* and *Glatzmaier* recommend removing hydrogen from the HTF system via the expansion vessel [4,5,8]. In contrast to these publications the removal of hydrogen has been practically tested within the present study in CSP plants by simply applying decompression of the HTF system after cooling down during the night. By this measure dissolved gases are released through the ullage and the exhaust gas treatment system to the atmosphere. Fresh nitrogen is fed into the system before the plant is heated up again.

According to figure 6 the HTF temperatures on the three test days were rather low and did not exceed about 360°C. On the third day the temperature at the field outlet even did not rise above 250°C. Hence, hydrogen formation had been low on each day, i.e. the hydrogen concentration had been more or less constant within an individual day.

Due to the massive gas release during the night the concentration of dissolved hydrogen was reduced by 30-50% from day to day. After two nightly decompressions the concentration was reduced to below 10μmol/kg starting at about 30μmol/kg on the first day. The test indicates that the hydrogen concentration can be lowered considerably using ready available system components.



**FIGURE 6.** Hydrogen concentrations in a CSP plant on three consecutive days. During the night the HTF system had been decompressed to release as much dissolved gas as possible (points: hydrogen, lines: temperature).

## CONCLUSION

Even though the formation of hydrogen due to the degradation of HTF is basically known, the need of hydrogen control is not yet communicated very well to the CSP plant operators. In this study it could be shown that under regular operation conditions the hydrogen concentration exceeds significantly the maximum allowed limit that was set for the Schott PTR<sup>®</sup> 70 receiver. Currently, no selective hydrogen removal techniques are validated for parabolic trough systems, and alternative HTFs with less hydrogen formation potential like silicone based HTFs are not yet broadly applied [7]. As long as no major technical changes are established in current CSP plants approaches using readily available techniques and components can be applied to avoid extremely high hydrogen levels. A promising approach is the frequent partial nitrogen exchange from the HTF system and a monitoring of the hydrogen concentration using off-line analysis of HTF samples in steel cylinders.

## ACKNOWLEDGMENT

Parts of this work have been funded by the German Federal Ministry for Economic Affairs and Energy, reference no. 0325288B, 0324216A, 0325845B, 0325846A and 0324235A.

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